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(54) **POLYMERES HYDROSOLUBLES OU GONFLABLES DANS  
L'EAU**

(54) **WATER-SOLUBLE OR WATER-SWELLABLE POLYMERS**

(57) TRANSLATION NOT AVAILABLE AT THIS  
TIME

(57) The present invention relates to water-soluble or water-swellaable polymers based on 2-acrylamido-2-methylpropanesulfonates, their preparation and their use for increasing the viscosity of aqueous solutions.



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**Abstract:**

**Water-soluble or water-swellaable polymers**

The present invention relates to water-soluble or water-swellaable polymers based on 2-acrylamido-2-methylpropanesulfonates, their preparation and their use for increasing the viscosity of aqueous solutions.

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## Description

## 5 Water-soluble or water-swellaable polymers

The present invention relates to water-soluble or water-swellaable polymers based on 2-acrylamido-2-methylpropanesulfonates, their preparation and their use for increasing the viscosity of aqueous solutions.

10

For economic reasons or reasons relating to the application or stability, water- or solvent-containing multicomponent systems, such as solutions, emulsions or suspensions, are frequently adjusted to higher viscosities or are thickened. For example, by increasing the viscosity of the external or

15 internal phase of emulsions or suspensions, it is therefore possible to ensure that the time which elapses before the separation of the components of such a mixture can be substantially increased, this resulting in a longer shelf live. Increasing the viscosity also improves the uniform distributability of many products, in particular on uneven surfaces. This

20 applies in particular to skin care compositions and pharmaceutical ointments on the skin. In the case of many industrial products, such as wallpaper removers, paint removers or aircraft deicers, the high viscosity prevents premature run-off from the surface to be treated. The efficiency is increased by the more uniform distribution and longer duration of action.

25 In addition to the stated advantages with respect to applications, the high viscosity of a such preparations also has further advantages in the production, packaging, filling and storage as well as in transportation. From the safety point of view, the thickening of acidic media is particularly important here.

30

In general, the rheological properties during the preparation and/or formulation of cosmetic, pharmaceutical or industrial preparations constitute a decisive criterion for the use of these products in practice. The thickeners used should lead to sufficient thickening even when employed

35 in very small amounts. The color and basic properties of the medium to be

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thickened should not be changed.

The technical literature mentions a large number of different systems for adjusting the rheological properties of aqueous or solvent-containing systems, emulsions and suspensions. For example, cellulose ethers and other cellulose derivatives (for example carboxymethylcellulose and hydroxyethylcellulose), gelatine, starch and starch derivatives, sodium alginates, fatty acid polyethylene glycol esters, agar agar, tragacanth or dextrans are known. Synthetic polymers used are various materials, such as, for example, polyvinyl alcohols, polyacrylamides, polyacrylic acid and various salts of polyacrylic acid, polyvinylpyrrolidone, polyvinyl methyl ether, polyethylene oxides, copolymers of maleic anhydride and vinyl methyl ether and various mixtures and copolymers of the abovementioned compounds.

However, the stated thickeners have various disadvantages in use. Thus, for example, the cellulose derivatives or generally the materials based on natural raw materials and the formulations resulting therefrom are very susceptible to bacteria. In use, they are generally evident from the formation of unpleasant, "stringy" gels. Fatty acid polyethylene glycol esters tend to hydrolyze in the presence of water, and the resulting insoluble fatty acids cause undesired turbidity. Thickeners of natural origin (for example, agar agar or tragacanth) have greatly fluctuating composition depending on the origin.

25

1. DE-C-1.042.233 discloses the preparation of crosslinked copolymers which contain at least 25% by weight of a lower aliphatic  $\alpha,\beta$ -unsaturated carboxylic acid or of an anhydride of a lower, aliphatic unsaturated polycarboxylic acid, from 0 to 75% by weight of a monoolefinic monomer differing therefrom and from 0.1 to 30% (based on the weight of the monomer) of a crosslinking agent as polymerized units. A serious disadvantage of this process is that it leads only to polymers having free carboxyl groups. These compounds are only poorly water-soluble and therefore have poor

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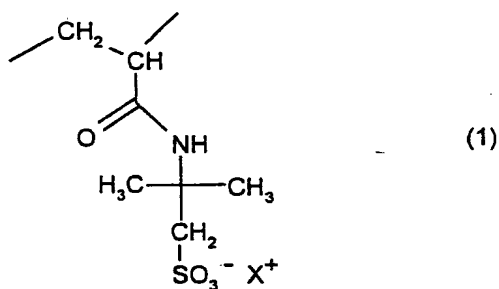
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swellability. In order to obtain highly swellable and readily thickening products, these products, which frequently have a viscous rubber-like consistency, must be macerated with alkali. This gives a gelatinous substance which can be adjusted to the desired viscosity by further addition of water. This involved process makes it considerably more difficult to use the thickeners described.

It is therefore the object of the present invention to provide thickeners which do not have the abovementioned disadvantages.

The present invention relates to water-soluble or water-swellaable polymers which contain, in random distribution, from 90 to 99.99% by weight of radicals of the general formula (1)



and from 0.01 to 10% by weight of crosslinking structures which are derived from monomers having at least two olefinic double bonds, where  $X^+$  is a cation or a mixture of cations and  $X^+$  may not comprise more than 10 mol % of protons ( $H^+$ ), and where the number of radicals of the general formula (1) in the polymer must be sufficiently large for the hydrodynamic volume of the polymers in aqueous solution to have a radius of from 10 to 500 nm and a homogeneous, monomodal distribution.

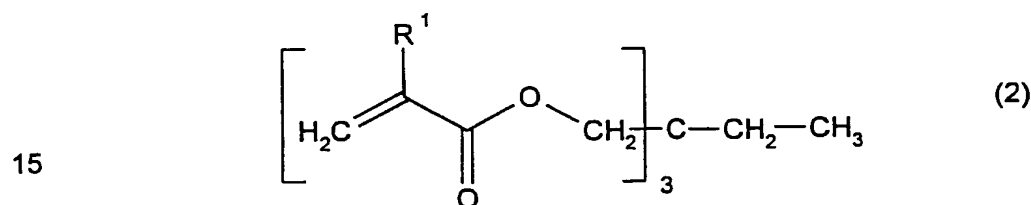
Preferred polymers according to the invention contain from 98 to 99.5% by weight of radicals of the general formula (1) and from 0.5 to 2% by weight of crosslinking structures which are derived from monomers having at least two olefinic double bonds.  $X^+$  is in particular a proton, a cation of an alkali metal, one equivalent of a cation of an alkaline earth metal or the ammonium ion. In preferred polymers according to the invention, 90-

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100 mol % of the cations  $X^+$  comprise ammonium ions ( $NH_4^+$ ) and from 0 to 10 mol % comprise protons ( $H^+$ ). Crosslinkable structures which are derived from monomers having at least two olefinic double bonds are preferably derived from, for example, dipropylene glycol diallyl ether, polyglycol diallyl ether, triethylene glycol divinyl ether, hydroquinone diallyl ether, tetraallyloxyethane or other allyl or vinyl ethers of polyfunctional alcohols, tetraethylene glycol diacrylate, triallylamine, trimethylolpropane diallyl ether, methylenebisacrylamide or divinylbenzene.

10 The crosslinking structures are particularly preferably derived from monomers of the general formula (2)



in which  $R^1$  is hydrogen or methyl.

20 The polymerization reaction described according to the invention gives not only linear chains but also branched and crosslinked polymer molecules. These molecules can be characterized by their rheological behavior in water and by the dynamic light scattering.

#### Rheological behavior

25 The rheological behavior is determined by a rheometer controlled by shear stress. A 1 percent strength by weight solution of the polymers is prepared and the shear stress is measured as a function of the shear rate. This measurement provides direct information about the performance characteristics. The shear rate-dependent viscosity is calculated as the  
30 quotient of shear stress and shear rate

$$\text{Viscosity} = \frac{\text{Shear stress}}{\text{Shear rate}}$$

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The dimensional stability or mechanical strength of the stationary, unstressed gel is measured at low shear rates, whereas the high shear rates correlate with the mechanical behavior under high stress, as, for example, during application and distribution of the gel on a substrate.

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Dynamic light scattering:

In the second possibility for characterization by dynamic light scattering, the distribution of the hydrodynamic volume of the polymer structures is measured. The dissolved macromolecules are flexible and are surrounded by a solvate envelope of water molecules. With charged polymers as in this case, the size of the macromolecule is greatly dependent on the salt content of the water. The identical charge along the polymer main chain leads to a considerable expansion of the polymer chain in polar solvents. By increasing the salt content, the electrolyte content of the solvent is increased and the identical charges are shielded from one another. In addition to the molecules transported in the solvate envelope, solvent molecules are also bonded in cavities of the polymer. The solvent molecules are then part of the macromolecule in solution and move at the same average velocity. The hydrodynamic volume then describes the linear dimension of the macromolecule and of these solvate molecules.

$$V_h = \frac{M}{N_A} (v_2 + dv_1)$$

	$V_h$	=	Hydrodynamic volume
25	$M$	=	Mass of the unsolvated macromolecule
	$N_A$	=	Loschmidt's constant
	$v_1$	=	Specific volume of the solvent
	$v_2$	=	Specific volume of the macromolecule
	$d$	=	Mass of solvent (in g) which is bonded to one gram of
30			unsolvated macromolecule

If the hydrodynamic particle is spherical, a hydrodynamic radius can be readily calculated from the hydrodynamic volume:

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$$V_h = \frac{4\pi R^3}{3}$$

R = Hydrodynamic radius

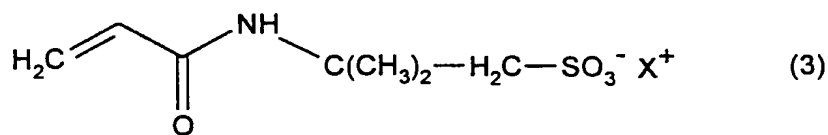
A hydrodynamic particle is an exact sphere only in very rare cases. Most synthetic polymers are coiled structures or highly eccentric ellipsoids. The stated radius is then based on a sphere frictionally equivalent to the body.

The equations so far apply only to the case of monodisperse polymer systems. In practice, however, distributions of molecular weights and hence also distributions of hydrodynamic radii and volume are always obtained. For polydisperse systems, the distribution of the diffusion coefficients must be calculated by means of a Laplace transformation of the integral equation (2). From this distribution, it is possible to obtain the distribution of radii and the distribution of the hydrodynamic volume.

The polymers according to the invention can be prepared by free radical polymerization of

a) 90 - 99.99% by weight of the 2-acrylamido-2-methylpropanesulfonate of the general formula (3)

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25

and

b) 0.01 - 10% by weight of one or more crosslinking agents which contain at least two olefinic double bonds.

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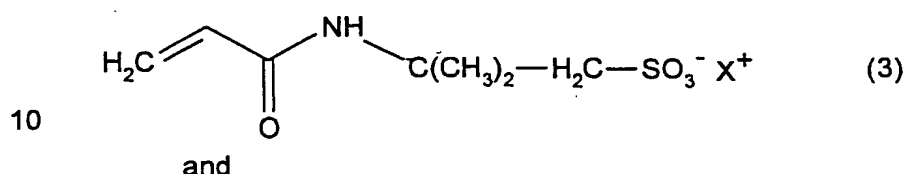


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The present invention also relates to water-soluble or water-swella-  
ble polymers which are obtainable by free radical polymerization of

- 5 a) 90 - 99.99% by weight of the 2-acrylamido-2-methyl-  
propanesulfonate of the general formula (3)



- b) 0.01 - 10% by weight of one or more crosslinking agents which  
contain at least two olefinic double bonds,
- 15 where  $X^+$  is a cation or a mixture of cations and  $X^+$  may not comprise more  
than 10 mol % of protons ( $H^+$ ) and where the hydrodynamic volume of the  
polymers in aqueous solution has a radius of from 10 to 500 nm and a  
homogeneous, monomodal distribution.

20 A preferred process for the preparation of the polymers according to the  
invention is a process wherein, for the preparation of the polymers,

- a.) from 90 to 99.99 parts by weight of the 2-acrylamido-2-  
methylpropanesulfonate of the general formula (3) is dissolved or  
25 dispersed in a solvent or solvent mixture, where  $X^+$  in this case may  
also comprise up to 100 mol % of protons;
- b.) if required, the solution or dispersion obtained according to a.) is  
neutralized by means of one or more bases to such an extent that at  
30 least 90 mol % of the sulfonic acid are converted into the salt form;
- c.) from 0.01 to 10 parts by weight of one or more crosslinking agents  
having at least two olefinic double bonds are added to the solution  
obtained according to a.) and b.), and

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d.) the polymerization is initiated in a manner known per se by compounds forming free radicals and is carried out at a temperature of from 10 to 150°C,

5 the choice of the solvent or solvent mixture mentioned in a.) being made so that the polymers obtained are substantially insoluble in this solvent or solvent mixture.

In a particularly preferred process of this type,

10

a.) from 98 to 99.5 parts by weight of the 2-acrylamido-2-methylpropanesulfonate of the general formula (3) are dissolved or dispersed in a solvent or solvent mixture, where  $X^+$  in this case may also comprise up to 100 mol % of protons;

15

b.) if required, the solution or dispersion obtained according to a.) is neutralized by means of one or more bases to such an extent that at least 90 mol % of the sulfonic acid are converted into the salt form;

20 c.) from 0.5 to 2 parts by weight of one or more crosslinking agents having at least two olefinic double bonds are added to the solution obtained according to a.) and b.), and

25 d.) the polymerization is initiated in a manner known per se by compounds forming free radicals and is carried out at a temperature of from 10 to 150°C,

the choice of the solvent or solvent mixture mentioned in a.) being made so that the polymers obtained are substantially insoluble in the solvent or  
30 solvent mixture.

The polymerization reaction is preferably carried out in a water-soluble alcohol or in a mixture of a plurality of water-soluble alcohols having from one to four carbon atoms, preferably in tert-butanol. The water content of

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the alcohol or of the mixture of the plurality of alcohols may not exceed 10% by weight since otherwise lumps may form in the course of the polymerization. Specifically, the choice of the type and of the amount of the solvent should be made so that the amount of 2-acrylamido-2-methylpropanesulfonic acid used and/or the salt to be polymerized are

5 substantially soluble or dispersible. Substantially soluble or dispersible is to be understood as meaning that no solid material settles out in the solution or dispersion even after the stirrer has been switched off. On the other hand, the polymer formed in the course of the reaction should

10 however be substantially insoluble in the chosen solvent (or solvent mixture). Substantially insoluble is to be understood here as meaning that a readily stirrable polymer paste in which no lumps or agglomerates may form is formed in the course of the polymerization. The filtrate obtainable by filtering off the paste with suction may have a solids content of not more

15 than 5% by weight. If the polymers are relatively highly soluble in the chosen solvent or solvent mixture, lumps may form during drying of the polymer paste.

The polymerization reaction itself is initiated in a manner known per se by

20 compounds forming free radicals, such as azo initiators (for example, azobisisobutyronitrile); peroxides (for example, dilauroyl peroxide) or persulfates, in a suitable temperature range from 20°C to 120°C, preferably from 40°C to 80°C, and is continued over a period of from 30 minutes to several hours.

25

#### Example 1:

2006.2 g of tert-butanol (97.5% strength, remainder: water) are initially introduced into a 5.0 l Quickfit flask having an anchor stirrer, a reflux condenser, an internal thermometer and an inlet facility for N<sub>2</sub> and NH<sub>3</sub>

30 (gaseous). Thereafter, 340.0 g of 2-acrylamido-2-methylpropanesulfonic acid are introduced and are dispersed with vigorous stirring, slight turbidity of the solvent persisting. 27-28 g of ammonia (gaseous, about equimolar with the 2-acrylamido-2-methylpropanesulfonic acid) are then passed into the gas space above over a period of about 30 minutes, and stirring is

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continued for a further 30 minutes at room temperature after or until a pH of  $6.0 \pm 0.5$  has been obtained. 32.0 g of TMPTA solution (trimethylpropane triacrylate) (25% strength in tert-butanol) are added and the mixture is heated at a temperature of  $T = 60^{\circ}\text{C}$ , the reaction mixture  
5 being blanketed by simultaneously passing in nitrogen. After the temperature of  $T = 60^{\circ}\text{C}$  has been reached, 4.0 g of DLP (dilauroyl peroxide) are added. The reaction is initiated immediately after the addition of the initiator, this being evident from an increase in the temperature and from the flocculation of the polymer. About 15 minutes after the  
10 beginning of the polymerization reaction, the nitrogen feed is stopped. About 30 minutes after the addition of the initiator DLP, the temperature reaches a maximum (about  $65-70^{\circ}\text{C}$ ). A further 30 minutes after passing through this maximum, the mixture is heated to the reflux temperature and stirring is continued for 2 hours under these conditions. The content of the  
15 reaction vessel assumes a pasty consistency in the course of the reaction but is still readily stirrable. The mixture is then cooled to room temperature and the solid is filtered off with suction. The paste is dried at  $60-70^{\circ}\text{C}$  for 24 hours in a vacuum drying oven. 391.0 g of a fine white powder are obtained.

20

The powder is dried and is dissolved in distilled water in an amount of 1.0% by weight. The firm, clear gel formed is outstandingly suitable as a thickener for aqueous solutions. The gels prepared using this thickener are suitable in particular for cosmetic applications since they give rise to a  
25 pleasant sensation on the skin when distributed over the body.

#### Example 2:

Example 1 is repeated, except that only 19.2 g of 25% strength TMPTA solution are added after the neutralization by ammonia.

30

The rheological behavior of gels prepared in this manner is determined as follows in a rheometer controlled by shear stress:

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## Apparatuses used:

1. Rheometer controlled by shear stress
2. Stainless steel plate/plate measuring geometry (diameter: 20 mm)
3. Infrared dryer with:
  - 5 - balance and
  - chart recorder
4. Mortar and pestle
5. 100 ml glass container with screw closure

## 10 Sample preparation:

About 1.5 g of the pulverulent material are finely ground in the mortar and dried for 15 minutes at 120°C in the infrared dryer. An exactly 1.0% strength gel of the dried material in demineralized water is prepared in a clean glass container with a screw cap:

15

Weighing: Weigh in 0.50 g of the sample and make up to a total weight of 50.00 g with demineralized water

- 20 The sample is allowed to stand until a homogeneous, optically transparent gel forms.

- The sample material is applied as uniformly as possible in the gap between the plates of the rheometer controlled by shear stress. If too much or too little material is present in the gap, the sample should be applied again. An initial torque is then applied so that a shear rate of  $5 - 10 \text{ s}^{-1}$  is obtained. Typically, a torque of 400 - 600 N is required. At this rotational velocity, the air bubbles present in the sample are removed by shear strength. Further sample material must be carefully added at the edge of the plate so that a perpendicular meniscus forms there.
- 25
- 30

If sample material is missing between the plates or too much is present, the sample slides on the plate and an irregular curve is obtained.

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The flow curve and velocity curve are recorded for the sample in a shear rate interval of from about  $0.01 \text{ s}^{-1}$  to  $15 \text{ s}^{-1}$ . The measurement is carried out three times altogether on each sample, the material remaining between the plates for all three measurements.

5

All three measurements must have the same curve qualitatively and may differ quantitatively from one another by about 5%.

First, the viscosity is determined at a shear rate of  $10 \text{ s}^{-1}$ . For the evaluation, only the third measurement is chosen. Furthermore, a complete viscosity curve is used. For this purpose, the logarithm to the base of 10 of the viscosity is plotted along the ordinate against the logarithm to the base of 10 of the shear rate.

For Examples 1 and 2, both of which may be used as thickeners, the following measurement result is obtained:

Result of the rheological investigations:

Results of the measurements of the experiments controlled by shear stress

20

Sample designation	Viscosity at a shear rate of 0.1 Hz in Pa·s	Viscosity at a shear rate of 10 Hz in Pa·s
Example 1	1040	30
Example 2	312	16

The hydrodynamic radius of the particles is determined by dynamic light scattering.

Physical background:

The dynamic light scattering determines the time-averaged intensity autocorrelation function of the scattered light/1,2/:

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$$G^{(2)} = \langle |I(t, q) / I(0, q)| \rangle = A [1 + B |g^{(1)}(q, t)|^2] \quad (1)$$

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where A is the measured base line,  $\beta$  is a coherence parameter, t is the correlation time and q is the scattering vector. In a polydisperse system, the normalized correlation function of the electric field strength  $g^{(1)}(q,t)$  is composed of the components in the scattering volume /3/

5

$$g^{(1)}(q,t) = \int_0^\infty G(\Gamma) \exp(-\Gamma t) d\Gamma \quad (2)$$

10 From the line width  $\Gamma$ , it is possible with the aid of the Stokes-Einstein diffusion coefficient to calculate the hydrodynamic radii of the components involved:

$$15 \quad \frac{\Gamma}{q^2} = D = \frac{kT}{6\pi\eta R} \quad (3)$$

where k is the Boltzmann constant, T is the absolute temperature in degrees Kelvin,  $\eta$  is the viscosity of the solvent (water) and R is the hydrodynamic radius of the components involved.

20

The determination of the line width from the field autocorrelation function is carried out with the aid of CONTIN /3,4,5/

Sample preparation:

25 The reaction product of the precipitation polymerization is dried for 24 hours at 70°C in a vacuum drying oven until the weight remains constant. A 0.01 percent strength by weight solution in bidistilled water (conductivity 15 MΩ/cm) is prepared from this material. The solution is then diluted until  
30 the autocorrelation function of the electric field strength is independent of the concentration. This state is referred to as infinite dilution, and the movement of the polymers and polymer networks is undisturbed and diffuse. The determined autocorrelation function of the electric field strength is thus only a function of the components involved and their distribution.

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All the abovementioned equations apply only to the case of infinite dilution of noninteracting particles.

Apparatus for dynamic light scattering:

- 5 A commercially available apparatus for dynamic light scattering /6/ has the following design:
- (ALV/DLS/SLS 5000 F monomodal fiber compact goniometer system version A Dual Plus 532) with a commercially available Multiple-Tau hardware correlator /6/ and with an Nd-YAG solid-state laser /7/ (ELS
- 10 Model 140-0532-100) is used for the analysis of the particle size distribution, at a wavelength of 532 nm with an average power of 110 mW. The incident beam is vertically polarized (1:100) relative to the plane of scattering /1/. The analysis of the particle size distribution is possible only if  $\beta$  from (1) has a value very close to unity; in our experiment, it is 0.98 /8/.
- 15 Owing to the high coherence factor  $\beta$ , an analysis of very dilute samples is possible with a good signal/noise ratio, and this reduces the error of extrapolation to zero concentration to a minimum.

References:

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- 25 /4/ Provincher S.W.; *Comp. Phys.* **27**, 213, 1982
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- /6/ ALV Laservertriebsgesellschaft mbH, Robert Bosch Str. 47, D-63225 Langen, Germany
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Using the method described above, the following values were obtained for the hydrodynamic radius of the main component of Examples 1 and 2, determined by dynamic light scattering:



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Example 1: 440 nm

Example 2: 160 nm

5 Example 3:

Example 1 is repeated, except that no solution of crosslinking agent (TMPTA solution) is added after the neutralization by ammonia.

10 The viscosity of a 1.0% strength by weight aqueous solution of Example 3 has a viscosity of 0.035 Pa·s at a shear rate of  $10 \text{ s}^{-1}$ . The viscosity achieved is therefore lower by a factor of 100 (relative to Example 2) to 1000 (relative to Example 1). Owing to the low viscosity, such polymers are no longer suitable for efficient thickening of aqueous solutions, in particular for the preparation of a cosmetic formulation. Moreover, the  
15 solutions prepared from such unbranched, i.e. linear, polymers tend to be "stringy", which is troublesome particularly in the preparation of cosmetic emulsions. The measurement of the hydrodynamic volume gives the following result:

20 Hydrodynamic radius of the main component determined by dynamic light scattering:

Example 3: 5.5 nm (linear polymer)

25 Example 4 (metering variant):

160.0 g of distilled water are initially introduced and heated to 95°C. 221.2 g of a 50% strength aqueous solution of an AMPS sodium salt and at the same time (but from a separate vessel) 120.0 g of a 1.0% strength aqueous 2,2'-azobisamidinopropane dihydrochloride solution are then  
30 pumped in within two hours. After the end of the metering, stirring is continued with refluxing for a further hour. The solution thus obtained is then dried. The sample, too, is tested rheologically as described further above, and the hydrodynamic radius is measured by means of light scattering. The rheological investigation gives the following result:

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Result of the measurement of the experiments controlled by shear stress

	Sample designation	Viscosity at a shear rate of 0.1 Hz in Pa·s	Viscosity at a shear rate of 10 Hz in Pa·s
	Example 3	0.1	0.035
5	Example 4	0.25	0.009

Such materials can no longer be used as thickeners.

Furthermore, the hydrodynamic volume of such polymers in water is much  
10 too small.

Hydrodynamic radius of the main components, determined by dynamic  
light scattering:

Example 4: 7 nm (linear polymer)  
15

The superiority of the branched polymers described is evident in particular  
in the thickening of acidic solutions. A 1% strength aqueous solution (in  
distilled water) has a gelatinous consistency. This also applies to materials  
which are obtained according to Example 1 or Example 2. Commercial  
20 thickeners which are based on polymers of acrylic acid or derivatives  
thereof (e.g. Carbool 980) have viscosities of more than 30 Pa·s according  
to the measuring method described above, in 1% strength aqueous  
solution in the neutral or slightly alkaline range. However, their thickening  
capacity (or the measured viscosity) declines sharply with decreasing pH.

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However, the materials according to the invention which are described  
above can maintain their viscosity up to a pH of about 3.

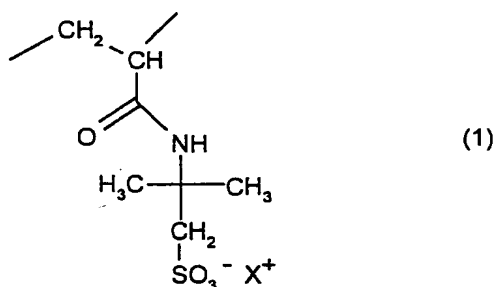
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## Patent Claims:

- 1.) A water-soluble or water-swellaible polymer which contains, in random distribution, from 90 to 99.99% by weight of radicals of the formula (1)



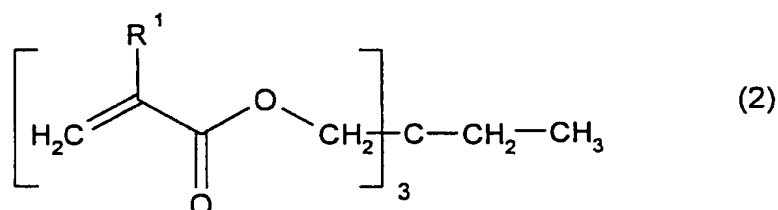
and from 0.01 to 10% by weight of crosslinking structures which are derived from monomers having at least two olefinic double bonds, where  $X^+$  is a cation or a mixture of cations and  $X^+$  may comprise not more than 10 mol % of protons ( $H^+$ ), and where the number of radicals of the formula (1) in the polymer must be sufficiently large for the hydrodynamic volume of the polymer in aqueous solution to have a radius of from 10 to 500 nm and a homogeneous, monomodal distribution.

- 2.) The water-soluble or water-swellaible polymer as claimed in claim 1, which contains 98 - 99.5% by weight of radicals of the formula (1) and from 0.5 to 2% by weight of crosslinking structures which are derived from monomers having at least two olefinic double bonds.
- 3.) The water-soluble or water-swellaible polymer as claimed in claim 1 and/or claim 2, wherein the crosslinking structures are derived from monomers of the formula (2)

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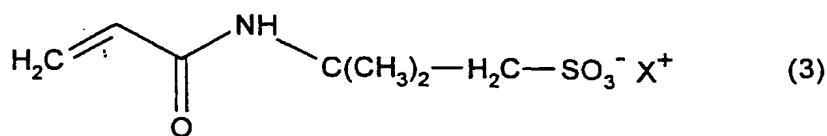
in which  $\text{R}^1$  is hydrogen or methyl.

10 4.) The water-soluble or water-swellaable polymer as claimed in one or more of claims 1 to 3, wherein 90 - 100 mol % of the cations  $\text{X}^+$  comprise ammonium ions ( $\text{NH}_4^+$ ) and from 0 to 10 mol % comprise protons  $\text{H}^+$ .

15 5.) A water-soluble or water-swellaable polymer which is obtainable by free radical polymerization of

a) 90 - 99.99% by weight of the 2-acrylamido-2-methylpropanesulfonate of the formula (3)

20



25

and

b) 0.01 - 10% by weight of one or more crosslinking agents which contain at least two olefinic double bonds,

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where  $\text{X}^+$  is a cation or a mixture of cations and  $\text{X}^+$  may comprise not more than 10 mol % of protons ( $\text{H}^+$ ) and where the hydrodynamic volume of the polymer in aqueous solution has a radius of 10 to 500 nm and a homogeneous, monomodal distribution.

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6.) A process for the preparation of the water-soluble or water-swella-  
ble polymers as claimed in one or more of claims 1 to 5, wherein, for  
the preparation of the polymers,

- 5           a.)    from 90 to 99.99 parts by weight of the 2-acrylamido-2-  
              methylpropanesulfonate of the formula (3) is dissolved or  
              dispersed in a solvent or solvent mixture, where  $X^+$  in this  
              case may also comprise up to 100 mol % of protons;
- 10          b.)    if required, the solution or dispersion obtained according to  
              a.) is neutralized by means of one or more bases to such an  
              extent that at least 90 mol % of the sulfonic acid are  
              converted into the salt form;
- 15          c.)    from 0.01 to 10 parts by weight of one or more crosslinking  
              agents having at least two olefinic double bonds are added to  
              the solution obtained according to a.) and b.), and
- 20          d.)    the polymerization is initiated in a manner known per se by  
              compounds forming free radicals and is carried out at a  
              temperature of from 10 to 150°C,

25           the choice of the solvent or solvent mixture mentioned in a.) being  
              made so that the polymers obtained are substantially insoluble in  
              this solvent or solvent mixture.

7.) The process as claimed in claim 6, wherein

- 30           a.)    from 98 to 99.99 parts by weight of the 2-acrylamido-2-  
              methylpropanesulfonate of the formula (3) is dissolved or  
              dispersed in a solvent or solvent mixture, where  $X^+$  in this  
              case may also comprise up to 100 mol % of protons;
- b.)    if required, the solution or dispersion obtained according to

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a.) is neutralized by means of one or more bases to such an extent that at least 90 mol % of the sulfonic acid are converted into the salt form;

5           c.)    from 0.5 to 2 parts by weight of one or more crosslinking agents having at least two olefinic double bonds are added to the solution obtained according to a.) and b.), and

10           d.)    the polymerization is initiated in a manner known per se by compounds forming free radicals and is carried out at a temperature of from 10 to 150°C,

15           the choice of the solvent or solvent mixture mentioned in a.) being made so that the polymers obtained are substantially insoluble in this solvent or solvent mixture.

20           8.)    The process as claimed in claims 6 and/or 7, wherein a solvent mixture comprising 90 - 100 parts by weight of one or more alcohols and 0 - 10 parts by weight of water is used, the alcohol used preferably being tert-butanol.

          9.)    The use of the polymers as claimed in one or more of claims 1 to 5 for thickening liquids.

25           10.)   The use as claimed in claim 9 for thickening liquids in a pH range of from pH 2.5 to 6.5, preferably in the pH range from 2.5 to 5.0.

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